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Polymer Composites for 3D Printing of Functional Sensors and Transducers

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Abstract—This paper represents a review of the recent work undertaken in the Digital and Materials Technology Laboratory at the University of Warwick on the theme of Additive Manufacturing (AM)/3D printing technology with polymer composites to carry out the manufacture of functional sensors and transducers. Examples of devices for acoustic, flow, electronic and chemical sensing are presented. Each sensor system utilizes a composite material developed in order to achieve functional sensing. This collection of examples demonstrates the viability of AM technology in the manufacture of bespoke sensor devices.

Keywords - 3D Printing; Additive Manufacturing; Stereolithography; Sensors; Transducers.

I. INTRODUCTION

Polymer-based additive manufacturing (AM) or 3D printing technologies such as Micro-stereolithography (MSL) and Fused Deposition Modeling (FDM) are part of a group techniques emergent from earlier rapid prototyping technologies which are receiving increased attention as enabling techniques for applications such as tissue engineering [1], microfluidics [2] and chemical reactors [3]. MSL utilizes photosensitive polymer resins, which are solidified using either a laser or projection light source in a layer-by-layer fashion. In this way a 3D object is built-up to replicate the structure of a digital design [4]. FDM employs extrusion of thermoplastic polymers to create a 3D filament network representing a digital design [5]. The tool-less and additive nature of AM technology offers considerable benefits over more traditional manufacturing processes. For instance, geometrically complex 3D structures can be quickly created in a matter of a few hours in order to meet specific demands.

There are a number of generally accepted benefits to the use of AM in certain applications:

- *Complexity is free*; in most cases there is no cost penalty to manufacturing a more complicated structure.
- *Variety is free*; a single manufacturing tool can make many different shapes and structures without new tooling.
- *Reduced lead-time*; components can be manufactured on-demand in response to requirements.

- *Reduced waste*; as little or no material is removed and material only placed where required, the amount of wastage is reduced.

While not an exhaustive list, the above benefits are of key interest in the manufacture of sensors or sensor systems, especially where low-volume, bespoke sensors are required. Until recently, technologies like FDM and MSL have only been used to produce components using simple polymers and polymer composites for structural applications (e.g. fixtures and molds).

Several methodologies can be adopted when considering the use of AM in relation to sensors, i) structures can be printed which improve the functionality of an existing sensor, ii) structures can be printed that undergo post-processing steps to achieve a functional sensor, iii) functional materials can be directly printed and then a sensor assembled (using a mixture of AM and non-AM parts or exclusively AM parts) or iv) multi-material direct printing, where functional materials are printed along with structural materials as part of the same process. All of these approaches can benefit from the geometric flexibility and tool-less nature of AM.

Exploring such methodologies for the manufacture of sensors poses a range of challenges, most notably in material development. For instance, adding capabilities such as electrical conductivity to printed objects often requires development of bespoke printable materials and material formulations. The most common route used to introduce functionality into 3D printable materials is through the incorporation of a filler material into an AM processable matrix such as a thermoplastic or thermoset polymer [6]. When incorporating such fillers however, considerations such as the filler volume fraction are particularly important as there is balance between achieving the desired functionality (e.g. overcoming percolation threshold in electrically conductive composites) and maintaining a viable processing window (e.g. minimising viscosity changes).

In this paper, the use of MSL and FDM for the production of acoustic transducers, flow sensors, electronic sensors and chemical sensors is presented. In each case, a printable functional material formulation is developed and used to manufacture a sensing device. The ability to rapidly take a design from a computer-aided design (CAD) to fabricated component using AM technology opens up many new research avenues in areas such as bespoke measurement and actuation.

II. ACOUSTIC

Ultrasound can be both generated and detected by use of a piezoelectric ceramic. Passing an alternating current through a piezo it causes it to vibrate at a high speed and to produce ultrasound *via* the piezoelectric effect [7].

A. Matching Layer Fabrication - MSL

A key problem in designing an efficient ultrasonic transducer for operating in a low acoustic impedance medium such as air, is the large impedance mismatch between the active piezoceramic material and the load medium. While acoustic matching layers can be added to the face of the piezoceramic, the associated manufacturing difficulties and reliability can impact upon the cost and longevity of the resultant transducer.

The use of AM techniques to add matching layers to a piezoelectric ceramic has thus been investigated and MSL has been used to print $\frac{1}{4}$ wave matching layers [8]. The layers are comprised of a photosensitive acrylic polymer resin, loaded with air-filled glass microballoons of diameter up to 140 microns (Fig. 1a). To avoid the use of a manual gluing step to attach the matching layer to the Lead Zirconate Titanate (PZT) transducer (a common failure point in a manufactured device), the layers were printed directly to the front face of the transducer (Fig. 1b). Fig. 1b shows the PZT transducer with wrap-around electrode and matching layer on front surface, designed for operation at 200 kHz.

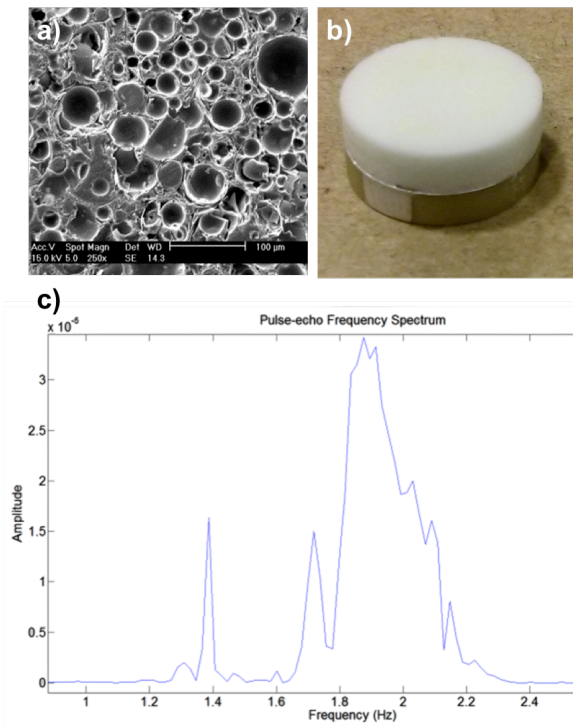


Fig. 1. a) Scanning electron microscopy image of printed matching layer, b) piezoelectric transducer with matching layer fabricated on the surface and c) pulse-echo frequency spectrum of a manufactured device.

The speed of sound in the matching layer material was found to be approximately 1865 m/s, and consequently the optimum quarter wavelength (QWL) matching layer thickness

for the filled matching layer was found to be 2.3 ± 0.1 mm for the specific PZT device considered in this paper. A pulse-echo experiment was carried out in order to characterise the devices (Fig. 1c) and showed a dominant frequency of 200 kHz. From tests against a conventional (glued and thinned) transducer, the results indicated that the MSL matching layer performance was comparable with the added advantage of very little raw material consumption, fine control over layer thickness, on-demand production and no manual intervention. *This is an example of using AM technology to improve the functionality of an existing sensor.*

B. Piezoelectric Ceramic Fabrication – MSL

Instead of using AM technology to adapt a piezoelectric transducer, MSL has also been used to manufacture piezoelectric elements directly [9]. *As an example of using AM technology to produce a structure that is post-processed to yield a functional sensor*, a photosensitive acrylic MSL resin was formulated and loaded with a piezoelectric material $0.65\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3 - 0.35\text{PbTiO}_3$ and used to produce a composite structure faithfully replicating a CAD representation (Fig. 2a and 2b respectively). After manufacture, the composite structure was thermally treated to remove the solidified polymer matrix and then heated at higher temperature (1250 °C held for 1.5 hours) to sinter the piezoelectric material. After thermal processing the components were found to have undergone uniform shrinkage of approximately 25% and yielded a dense ceramic of 97.5% density compared to the theoretical maximum (Fig. 2c).

2D piezoelectric arrays are of importance in medical imaging and non-destructive testing [10]. Utilizing our MSL approach, various shapes, sizes and array element geometries can potentially be investigated. Arrays comprising of pillars of circular cross-section could potentially find application in the reduction of cross-coupling between array elements. A laser vibrometer has thus been used to study this in a manufactured array by exciting one particular element (element 11) (Fig. 2d), and scanning the vibrometer onto other elements (7 and 13) in the array and measuring the vibration amplitude as a function of position (Fig. 2e, upper and lower respectively). It is evident that the cross-coupled signal reduces with distance away from the excited element. This is consistent with both mechanical and electrical cross-coupling. Further experiments would need to be performed to determine which of these is dominant, but the former is likely to be so. These results were performed using cylindrical array elements - an example of the flexibility of the MSL approach (these would be difficult to produce by more traditional fabrication methods).

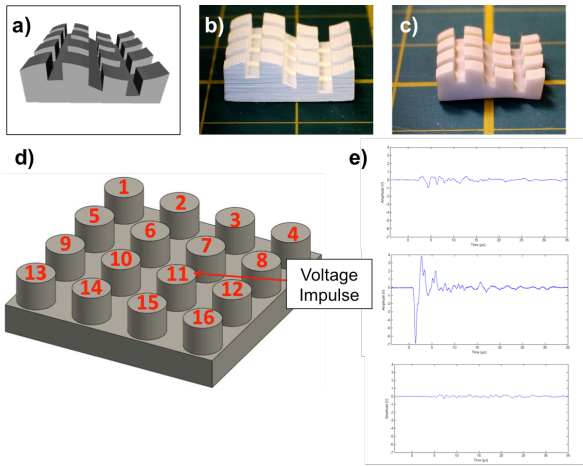


Fig. 2. a) Digital design for 2D array transducer (14.5 mm square), b) MSL manufactured composite, c) sintered device, d) schematic of circular pillar device and e) response at array elements 7, 11 and 13 (upper, middle and lower respectively).

Other piezoelectric devices have been built without tooling or recourse to additional equipment or processes, and have effectively detected and generated ultrasound in the MHz range [9]. The tool-less manufacture of 3D piezoelectric transducers with such a high degree of geometric freedom at such a high density and without impact upon the piezoelectric properties represents a significant development in the field of ultrasonics.

III. FLUID FLOW

The design of flow measurement systems represents an interesting engineering challenge, from design of the flow sensor itself to the development of transducers systems [11]. AM techniques have the potential to compress any development time for new sensor systems and provide a short lead-time solution for replacement of faulty or broken sensors.

A. Flow Sensor – MSL

In order to demonstrate the use of AM techniques in the production of flow measurement devices, a novel composite polymer resin for use with MSL systems was developed [12]. The resin incorporated a loading of magnetite nanoparticles, and provided a novel means to fabricate components with magnetic properties to provide a functional use within the built components. The developed material was used to print a magnetite composite impeller to sit inside a sensor body produced using a standard MSL resin material (Fig. 3a and 3b). The magnetic properties of the new material were used to produce a device that exhibits a rotating magnetic field whose frequency is proportional to the flow rate of a liquid through the device. The rotation (and therefore flow rate) is externally detected using a magnetic field sensor. Using this setup, the frequency of rotation of the flow sensor was recorded against the flow rate of water through the device (Fig. 3c). The printed device exhibited exceptional performance and with an approximately linear response to applied flow rate. By fabricating a bespoke flow sensor in this way, not only can the device be tailored to the needs of the system but it can be designed to integrate more compactly into an existing system.

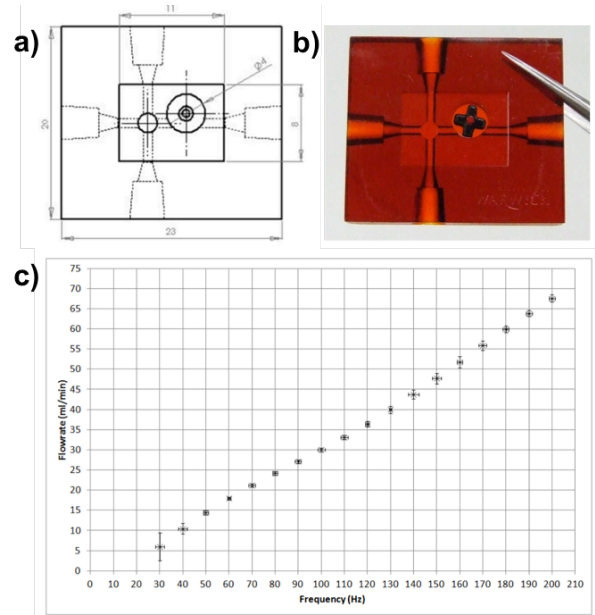


Fig. 3. a) Schematic of device designed, b) MSL manufactured device and c) response of device to increasing flow rate of water.

As the MSL process is relatively inexpensive, it provides a realistic method of fabricating such bespoke devices that can be iteratively modified or improved as needed.

B. Flow Sensor – FDM

Utilising the same operating principle as that employed for the production of a flow sensor *via* MSL, a flow sensor was also produced using FDM [13]. A sensor was designed as a direct replacement for a commercially available flow sensor, which detects impeller rotation *via* a hall-effect sensor. Magnetite nanoparticles (Fig. 4a) were dispersed in a polycaprolactone thermoplastic matrix *via* solution dispersion. The resultant composite was processed into a filament feedstock for a commercial desktop FDM system.

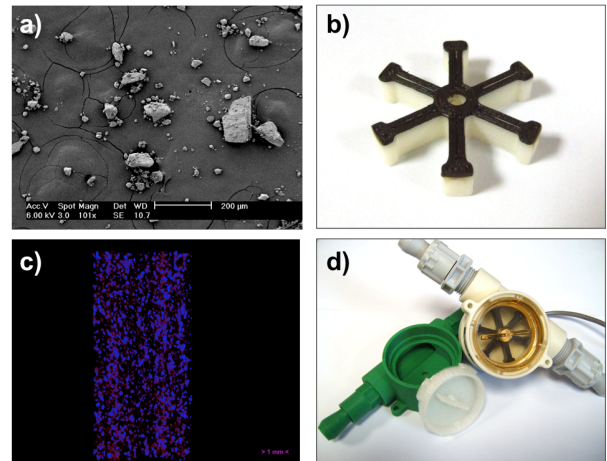


Fig. 4. a) Scanning electron microscopy image of as-received magnetite nanoparticles, b) FDM manufactured impeller, c) X-ray microfocus CT image showing dispersion of magnetite nanoparticles in impeller arm and d) FDM manufactured flow sensor (green) next to comparable commercial device.

Unlike the MSL flow sensor where the entire impeller was composed of functional material, the magnetite thermoplastic was used to add two layers of functional material to an Acrylonitrile Butadiene Styrene (ABS) printed impeller in the same print process using the multi-material capability of the FDM system (Fig. 4b). After manufacture of the impeller, X-ray microfocus computed tomography (CT) was used to assess the dispersion of magnetite nanoparticles in an arm of the impeller (Fig. 4c). The nanoparticles were evenly dispersed with no apparent clustering resultant from the extrusion process. When tested against the equivalent commercial sensor, the printed sensor showed good correlation. Both examples of flow sensors demonstrate the viability of AM technology for the rapid production of functional sensors. Using AM technology, designs can be iterated quickly or sensors replaced quickly with short lead times and complete flexibility in design. *Both of these devices are examples of directly printing functional materials for assembly into a sensor device.*

IV. ELECTRONIC

The incorporation of electronic circuitry inside objects produced by AM has long been an important developmental goal for AM technology [14]. The ability to embed circuitry and sensors inside objects during manufacture would allow the production of objects with levels of functionality not achieved by more traditional manufacturing processes.

To demonstrate the incorporation of functional sensors into AM manufactured devices, we formulated a simple conductive thermoplastic composite termed ‘carbomorph’ using carbon black (Fig. 5a and b) in a matrix of polycaprolactone. The carbon black particles were dispersed in the matrix *via* solution dispersion. The resultant composite was then formulated into a feedstock filament for a desktop FDM system with multi-material capability (Fig. 5c and d). The loading of carbon black within the polymer matrix was optimized so as to be easily printable by the desktop FDM without modification (Fig. 5e). Higher loadings of carbon black resulted in a composite with high melt viscosity that would not easily pass through the nozzle of the FDM system.

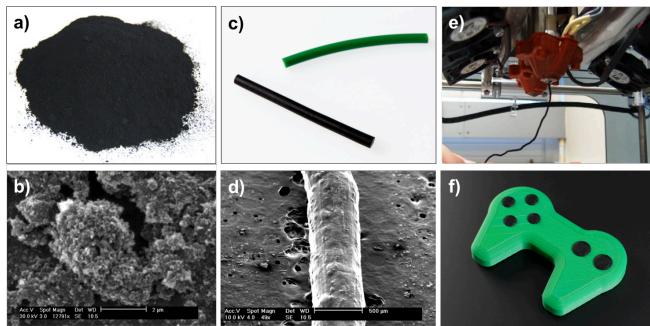


Fig. 5. a) Carbon black particles, b) scanning electron microscopy of carbon black particles, c) 3 mm composite feedstock filament (black), d) scanning electron microscopy image of carbon black composite filament, e) extrusion of composite through FDM nozzle and f) single print games controller using carbon black composite for capacitive touch sensing.

Once an optimum particle loading was found, the composite was used to produce components containing flex

sensors and capacitive sensors for fluid level sensing and for human-computer interface (Fig. 5f) [15]. The use of a multi-material capable FDM system with an electrically conductive material demonstrated the potential of AM technology for creating whole products incorporating sensors, without requirement for manual or lengthy assembly. *This is an example of multi-material direct printing, where functional materials are printed along with structural materials as part of the same process.*

V. CHEMICAL

There is wide interest in chemical sensing techniques, especially in gas and vapor sensing technologies covering a wide variety of applications including, environmental monitoring, process control and food safety [16,17]. To demonstrate the production of a functional chemical sensor using AM technology, a vapor sensor was selected as a target device [18]. Arguably the simplest method of vapor or gas detection is with the use of a chemical resistor (also often referred to as a Chemiresistor or Chemoresistor) which have the advantage of operating at room temperature. Common types of chemoresistors use conducting polymers and composite polymer materials. Typically, such devices are produced using screen-printing however such processes do not allow for complex 3D arrangements and architectures.

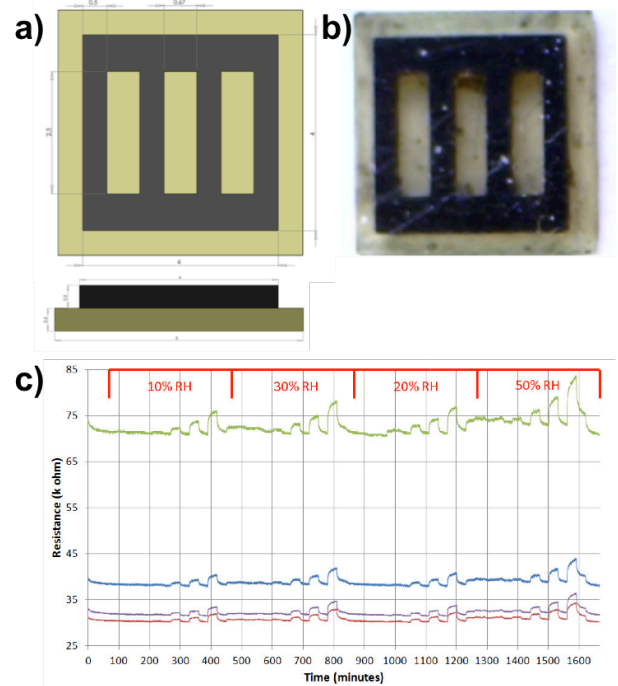


Fig. 6. a) Schematic of 5 mm x 5 mm sensing device, with 4 mm x 4 mm sensing region, b) photograph of manufactured device, c) response of a set of various sensors to ethanol vapor at different relative humidity (RH) values.

To create a chemiresistive material, carbon black particles were dispersed in a custom formulated polyethylene glycol (PEG) based photosensitive MSL resin. Using a custom-built multi-material MSL system, the material was used to produce

a multilayer device comprising of a PEG resin base and carbon composite functional layer (Fig. 6a and b). After manufacture, the devices were connected to a custom-built measurement circuit and vapor test rig and exposed to a range of chemical vapors. The devices showed good responses to the vapors with viable response rates and temperature dependence. Using AM technology to produce chemical sensors would allow sensors to be embedded inside objects such as lab-on-a-chip devices during manufacture or easily placed on the surface of devices for environmental detection. *Again, this is an example of multi-material direct printing, where functional materials are printed along with structural materials as part of the same process.*

CONCLUSIONS

A range of sensors produced using AM techniques in unison with specially developed polymer composite materials has been presented. The use of AM technology allows for rapid development and deployment of sensors, while facilitating the ability to adopt a range of architectures and geometries. Furthermore, AM technology allows sensors to be incorporated inside and as part of products and components during manufacture. Work is ongoing to further improve the functionality of manufactured devices and establish a full range of printable functional materials.

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REFERENCES

- [1] S.J. Hollister, "Porous scaffold design for tissue engineering.", *Nature materials* vol. 4, 518-524, 2005.
- [2] A.K. Au, W. Lee, and A. Folch, "Mail-order microfluidics: evaluation of stereolithography for the production of microfluidic devices.", *Lab on a Chip*, vol. 14, 1294-1301, 2014.
- [3] A.J. Capel, S. Edmondson, S.D. Christie, R.D. Goodridge, R.J. Bibb, and M. Thurstans, "Design and additive manufacture for flow chemistry.", *Lab on a Chip*, vol. 13, 4583-4590, 2013.
- [4] A. Bertsch, S. Jiguet and P. Renaud, "Microfabrication of ceramic components by microstereolithography.", *Journal of micromechanics and microengineering*, vol. 14, 197-203, 2004.
- [5] I. Zein D.W. Hutmacher, K.C. Tan, S.H. Teoh, "Fused deposition modeling of novel scaffold architectures for tissue engineering applications.", *Biomaterials*, vol. 23, 1169-1185, 2002.
- [6] M.L. Shofner, K. Lozano, F.J. Rodríguez-Macias and E.V. Barrera, "Nanofiber-reinforced polymers prepared by fused deposition modeling.", *Journal of applied polymer science*, vol. 89, 3081-3090, 2003
- [7] J.A. Gallego-Juarez, "Piezoelectric ceramics and ultrasonic transducers.", *Journal of Physics E: Scientific Instruments*, vol. 22, 804, 1989.
- [8] S.N. Ramadas, M. Hunter, J. Thornby, C.P. Purcell, S.J. Leigh and S.M. Dixon, "Additive manufacture of impedance matching layers for air-coupled ultrasonic transducers", unpublished.
- [9] D.I. Woodward, C.P. Purcell, D.R. Billson, D. A. Hutchins, and S.J. Leigh. "Additively-manufactured piezoelectric devices." *Physica status solidi (a)*, 2015.
- [10] N. Remi, M. Lejeune and T. Chartier, "3D fine scale ceramic components formed by ink-jet prototyping process.", *Journal of the European Ceramic Society*, vol. 25, 2055-2059, 2005.
- [11] H. Liu, S. Zhang, R. Kathiresan, T. Kobayashi, and C. Lee, "Development of piezoelectric microcantilever flow sensor with wind-driven energy harvesting capability.", *Applied Physics Letters*, vol. 100, 223905, 2012.
- [12] S.J. Leigh, C.P. Purcell, J. Bowen, D.A. Hutchins, J.A. Covington and D.R. Billson, "A miniature flow sensor fabricated by microstereolithography employing a magnetite/acrylic nanocomposite resin.", *Sensors and Actuators A: Physical*, vol. 168, 66-71, 2011.
- [13] S.J. Leigh, C.P. Purcell, D.R. Billson and D.A. Hutchins, "Using a magnetite/thermoplastic composite in 3D printing of direct replacements for commercially available flow sensors.", *Smart Materials and Structures*, vol. 23, 095039, 2014.
- [14] A.J. Lopes, E. MacDonald and R.B. Wicker, "Integrating stereolithography and direct print technologies for 3D structural electronics fabrication.", *Rapid Prototyping Journal*, vol. 18, 129-143, 2012.
- [15] S.J. Leigh, R.J. Bradley, C.P. Purcell, D.R. Billson and D.A. Hutchins, "A simple, low-cost conductive composite material for 3D printing of electronic sensors", *PLOS ONE*, vol. 7, e49365, 2012.
- [16] F.J. Santos and M.T. Galceran, "Modern developments in gas chromatography-mass spectrometry-based environmental analysis.", *Journal of Chromatography A*, vol. 1000, 125-151, 2003.
- [17] M. Penza, G. Cassano, F. Tortorella and G. Zaccaria, "Classification of food, beverages and perfumes by WO₃ thin-film sensors array and pattern recognition techniques.", *Sensors and Actuators B*, vol. 73, 76-87, 2001.
- [18] C.P. Purcell, J.A. Covington and S.J. Leigh, "Additive manufacture of vapour sensors via projection microstereolithography", unpublished.